EXHIBIT A179

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MEASUREMENT OF THE THICKNESS OF AMPHIBOLE ASBESTOS FIBERS WITH THE SCANNING ELECTRON MICROSCOPE AND TRANSMISSION ELECTRON MICROSCOPE

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Knowledge of the cross-sectional shape of mineral fibers is important for their accurate dimensional characterization. Two techniques for the measurement of width and thickness of fibers are described and compared: one for the scanning electron microscope (SEM), and one for the transmission electron microscope (TEM). The frequency distributions of log thickness and log width determined by these techniques are considerably more accurate when the TEM is used. However, the use of either technique results in essentially the identical quantitative descriptions of the relationship between thickness and width for amosite and crocidolite. A general relationship between thickness and width for amphibole asbestos is log thickness = 0.692 log width - 0.493; a rectangle is a reasonable approximation of its cross-sectional shape.

The Particulate Mineralogy Unit of the Bureau of Mines, Department of the Interior, concerned with the accurate characterization of minerals. Recent studies include the characterization of mineral fiber populations for health-related studies and mineral particles found in both the occupational and nonoccupational environment. The dose of mineral fibers for biological experimentation and the human exposure to mineral fibers from air or water are usually expressed in some unit of mass such as fibers pers microgram,[1-3] or nanograms per cubic meter.[4-6] In order to establish these values of concentration, either the thickness of the mineral fibers must be derived or measured, or some reasonable model for the cross-sectional shape of the fiber must be assumed so that volume can be calculated from the measurements of length and width alone. The purposes of this study were (1) to compare and evaluate two methods of measuring the thickness of mineral fibers by electron microscopy, and (2) to propose a reasonable model for the cross-sectional shape of amphibole asbestos.

Sample Preparation

Two samples of asbestos, one of amosite and the other of crocidolite, were examined. Both have been extensively characterized.[7-8] Microgram quantities of each sample were briefly sonicated in filtered distilled water. Drops of the suspensions were placed on highly polished brass SEM stubs and on 200-mesh Formvar and carbon-coated copper TEM grids. Over 99% of the fibers settle out of suspension with their smallest dimension normal to the surface of the substrate. A drop of filtered distilled water containing tiny glass spheres was added to the brass stubs; grids containing only glass spheres were also prepared. The brass stubs were coated with AuPd to a maximum thickness of approximately 200 Å. The TEM grids were placed in rows on a glass slide about 7 cm from a source of AuPd and at an angle to it of about 30° from the horizontal. They were then coated to a maximum thickness of 175 Å .

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Experimental Technique

Scanning Electron Microscope. All SEM measurements were made on an ISI Model 60 operated in a backscatter mode with a Taylor Engineering Combination Electron Detector. (Reference to specific trade names or equipment does not imply Bureau of Mines endorsement.) The technique used to measure thickness was first suggested to us by Daniel Baxter, Science Applications Laboratory, La Jolla, Calif. The detector is employed in a low angle position in the plane of sample tilt (Fig. 1). The working distance is set at 14 mm, and the sample is tilted through angle ϕ (in this study $\phi = 45°$). The instrument is operated at 20 kV and maximum spot size. In this configuration, "shadows" are formed along the edges of particles because the particles prevent the directional backscattered electrons from reaching the detector (Fig. 2).

According to the geometric arrangement shown in Fig. 1, the length Sm of the shadow as measured on the cathode ray tube (CRT) is related to the thickness of the particle by

$$h = \frac{Sm \sin \theta}{\cos(\phi - \theta)} \tag{1}$$

where θ is established from the measurement of the radius r and shadow length S_c of the small glass spheres (Fig. 3) by the relationship

$$\tan \frac{\theta}{2} = \frac{r \cos \phi}{S_c + r(1 - \sin \phi)} \tag{2}$$

In this study $\theta \simeq 15°$. The shadow must always be measured in the plane perpendicular to the axis of tilt. This plane contains the beam and the axis of the detector. On the ISI 60, the trace of the plane on the CRT is vertical. The direction of the trace of this plane on other instruments can be established from the direction of shadow elongation of the glass spheres. As long as the fibers are aligned parallel to this direction on the CRT, the measured width W_m is a direct measurement of true width W. However, if the fibers are horizontal, W_m is related to W by

$$W = \frac{W_m}{\cos \phi} \tag{3}$$

If the particle makes an angle γ with the vertical, then the relationship becomes

$$W = W_m \sqrt{\cos^2\gamma + (\sin^2\gamma/\cos^2\phi)} \tag{4}$$

Equation (4) is derived from the equation for an ellipse, where the long axis is the true width W, the short axis is the measured width with maximum foreshortening ($W \cos \phi$), and γ is the angle a radius makes with the long axis of the ellipse. This elliptical relationship is discussed by Boyde.[9]

All measurements were made at 10 000×. It was found that at higher magnification, it became increasingly difficult to determine the shadow boundaries, and no increase in precision was gained by an increase in magnification. Consequently, there is a lower limit on width and shadow length measurements of 0.10 µm, and the smallest thickness that could be calculated is approximately 0.05 µm. In fact, there did not appear to be any shadows at all from most fibers less than 0.15 µm wide.

The widths and thicknesses were calculated from W_m, γ, θ, and S_m for 160 amosite fibers and 128 crocidolite fibers. The data were collected by measurments on all nontouching fibers in randomly selected fields of view.

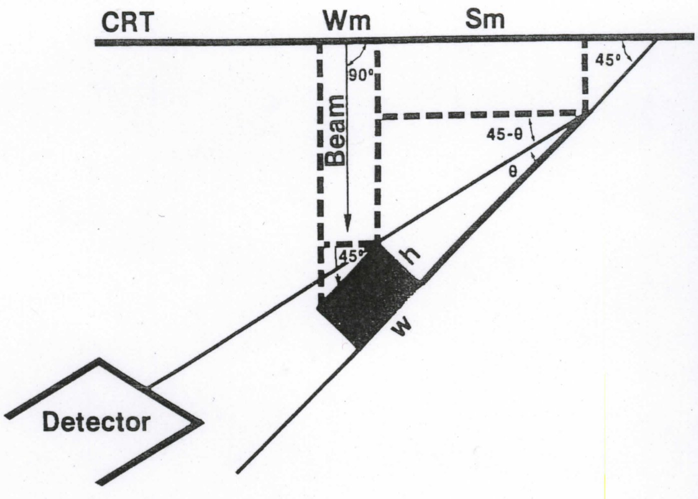

FIG. 1.--Sample, detector and beam positions for SEM technique. S_m is shadow length measured on cathode ray tube (CRT), W_m is measured width, angle of sample tilt $\phi = 45°$, W is true width, h is thickness, and θ is angle between axis of detector and surface of specimen stub.

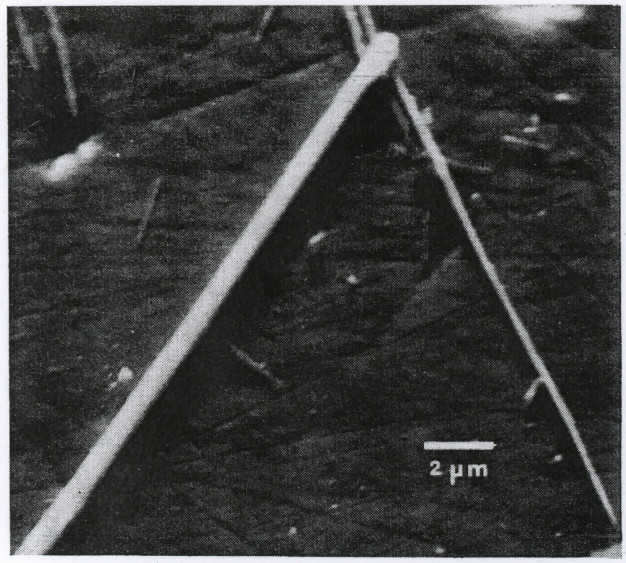

FIG. 2.--Shadows formed on crocidolite fibers on SEM.

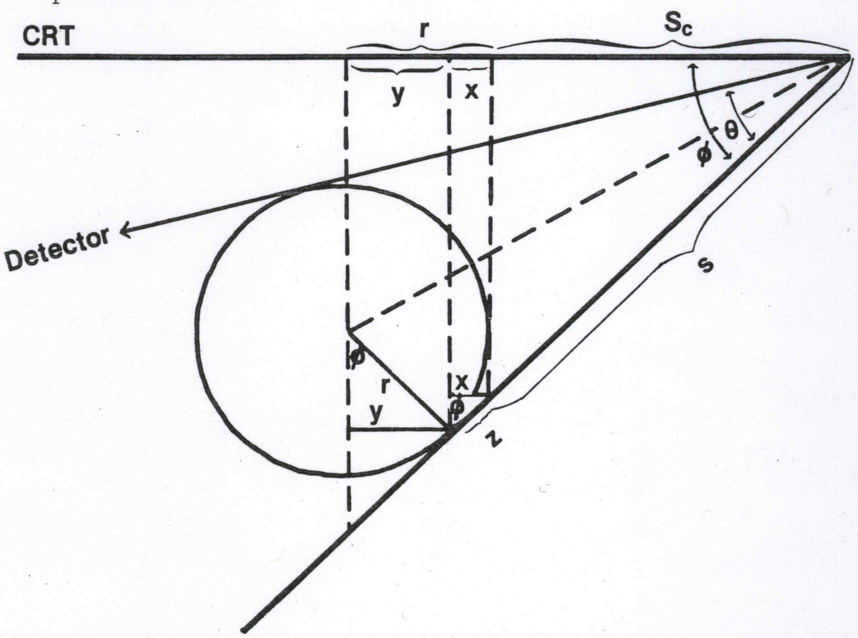

FIG. 3.--Geometric relationships for the calculation of θ: r = radius of sphere, ϕ = angle of sample tilt (in this study $\phi = 45°$); θ = angle between the detector axis and the surface of the specimen stub (in this study, $\theta \simeq 15°$); S_c = projection of the shadow S on the cathode ray tube (CRT).

Transmission Electron Microscope. The technique we used to measure thickness on the TEM is well established.[10] The low-angle coating of the grids by AuPd produces a clearly visible "shadow" whose length Sl is related to the thickness of the particles t and the coating angle α by the relationship

$$t = Sl \tan \alpha \qquad (5)$$

In this case the "shadow" is formed because the particles block the AuPd during the coating process. The value of α is established from the radii r and from the shadow lengths measured from the center of the glass spheres Sl by the relationship

$$\tan \frac{\alpha}{2} = \frac{r}{Sl} \qquad (6)$$

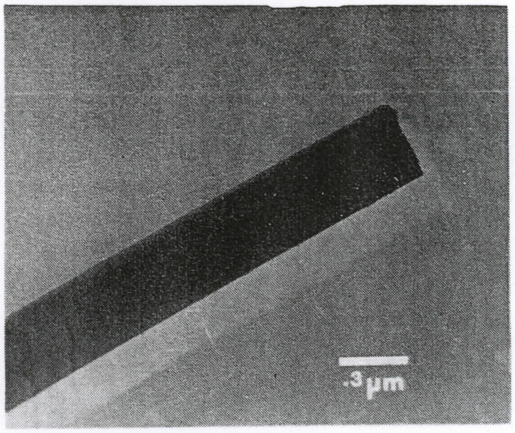

FIG. 4.--Amosite fiber and shadow formed by absence of AuPd coating.

S1 must be measured in the direction of the AuPd source. This direction is easily established from the shadow pattern at the end of the fibers (Fig. 4).

The width and shadow lengths of 143 crocidolite fibers and 150 amosite fibers were measured and thicknesses calculated. All measurements were made at 37 000× directly from the CRT on a Hitachi Model H600 scanning transmission electron microscope.

Results

A statistical description of the populations of width and thickness is given in Table 1. Frequency distributions of log width and log thickness are plotted in Fig. 5. A least-squares linear regression analysis of the form log thickness (μm) = F log width (μm) + b was conducted. The regression coefficients F and b, the standard error of the estimate, and the correlation coefficient r are also given in Table 1. Figure 6 is a plot of these least-squares linear regressions.

Discussion

From Table 1 and Fig. 5, it is evident that larger particles were measured by means of the SEM technique. Not only are the mean widths and thicknesses greater, but the frequency distributions are skewed, which reflects the omission of smaller particles in the measurements. This bias is a result of the inherently lower resolution of the SEM compared to the TEM and to the specific operating conditions of the SEM for this technique. Spot size, backscatter mode, working distance, operating voltage, and collection efficiency of the detector affect the resolution. These parameters were optimized for shadow visibility rather than resolution. Also, fibers less than about 0.15 μm wide were not measured on the SEM because shadows were not visible on these thin fibers.

Figure 6 and Table 1 present the results of the least-squares linear regression analyses. There is a remarkable similarity in the regression coefficients from the four analyses. Wylie and Schweitzer[11] discuss the variability of the values of F and b relating log width to log lenght for the mineral wollastonite. They conclude that values of F derived from populations of 250 particles whose ranges and standard errors are comparable to our data are statistically indistinguishable if they differ by no more than 0.22. Considering that the sample sizes of our populations are much smaller than 250 and that the maximum difference in F is 0.18, there are probably no significant differences among the four analyses. This result implies that for all practical purposes, either technique can be used to obtain the regression relationship relating thickness to width--even though the regression equations are derived from different segments of the fiber populations. Therefore, all data can be combined to give a general regression relationship for amphibole fibers of the form

$$\log \text{thickness} = 0.692 \log \text{width} - 0.493 \tag{7}$$

Although both techniques used in this study resulted in the same regression relationship between thickness and width, there are strong arguments to be made in favor of the TEM technique for the characterization of asbestos. First, the range of widths measured was greater when this technique was used. In general, the larger the range in the measurements, the more "well fixed" the regression line.[11] Second, the regression analysis is based on the assumption of normal distributions of log width and log thickness. The skewness of the distributions derived from the SEM technique could affect the usefulness of the regression coefficients as descriptive parameters. Third, the measurements of width and thickness on the TEM are more precise and are more likely to reflect the true

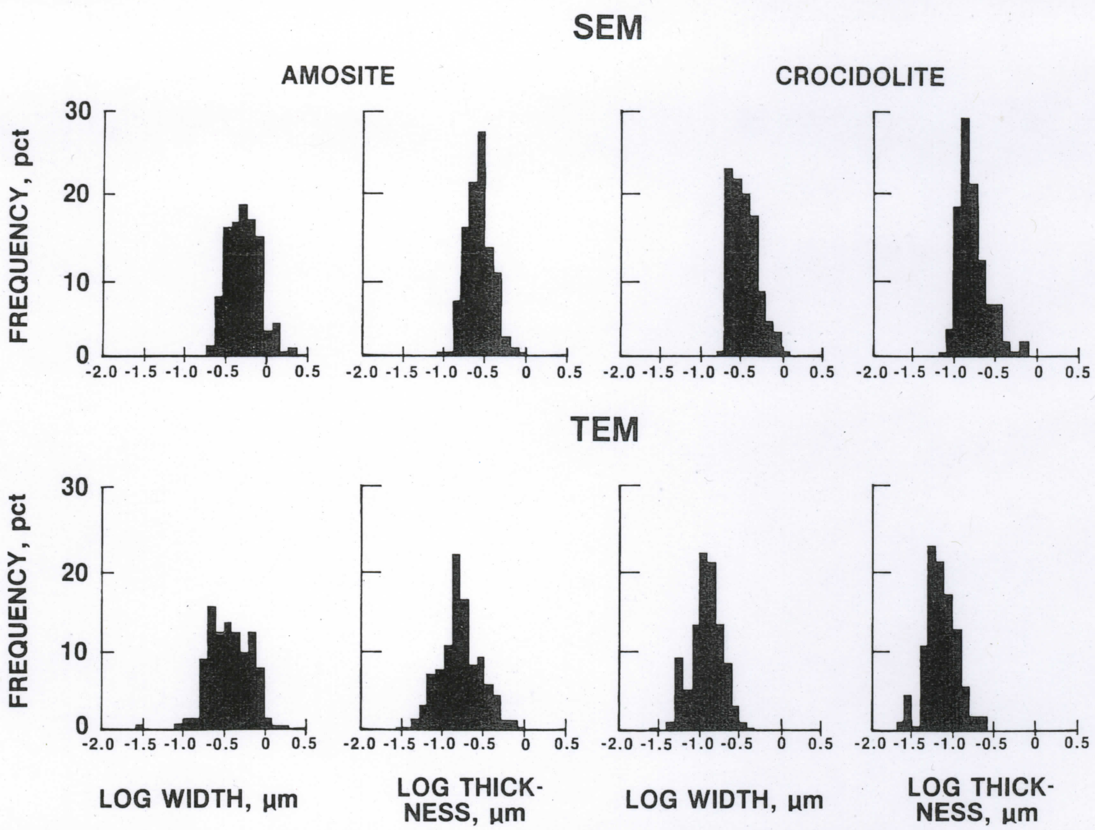

FIG. 5.--Frequencies of log width and log thickness obtained by SEM and TEM techniques.

TABLE 1

	Amosite (SEM)	Amosite (TEM)	Crocidolite (SEM)	Crocidolite (TEM)
Mean width (μm)[a]	0.55	0.35	0.35	0.12
Log width (μm)				
mean	-0.262	-0.453	-0.456	-0.922
standard deviation	0.186	0.270	0.174	0.208
minimum	-0.673	-1.355	-0.775	-1.569
maximum	0.230	0.205	0.048	-0.304
Mean thickness (μm)[a]	0.22	0.16	0.14	0.08
log thickness				
mean	-0.665	-0.802	-0.848	-1.112
standard deviation	0.165	0.266	0.199	0.198
minimum	-1.085	-1.784	-1.270	-1.592
maximum	-0.181	-0.022	-0.177	-0.564
Number of particles	160	150	128	143
Regression analysis $\log t = F \log w + b$				
F	0.607	0.792	0.729	0.724
b	-0.506	-0.443	-0.515	-0.445
standard error[b]	0.121	0.160	0.154	0.129
r[c]	0.686	0.802	0.638	0.760

[a]Geometric mean.
[b]Standard error of the estimate = $\sqrt{\text{variance}}$.
[c]Correlation coefficient.

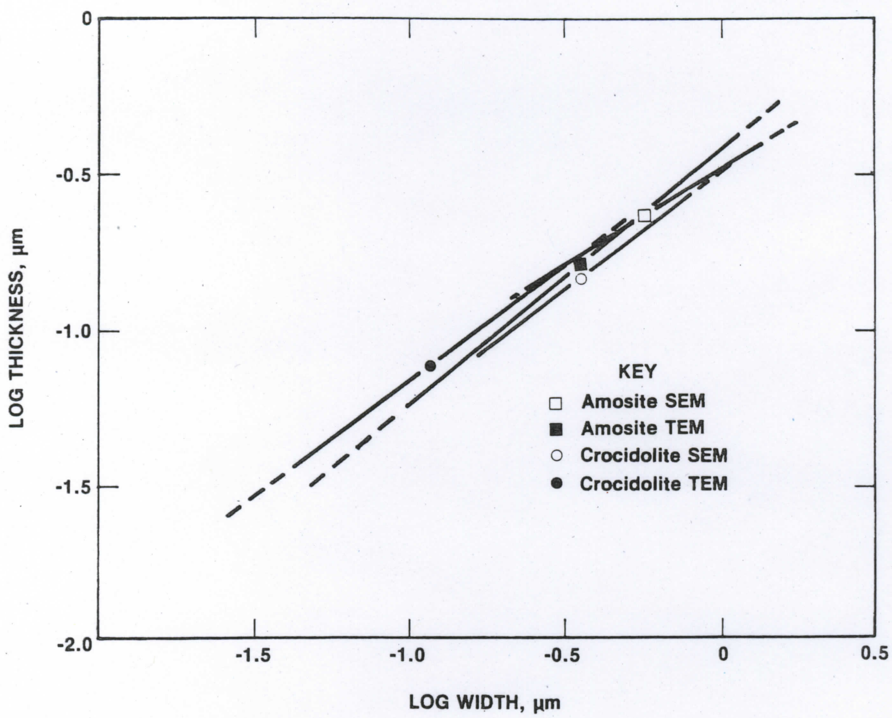

FIG. 6.--Plot of linear least-squares regression relationships between log thickness and log width. Mean log width for each is designated by appropriate symbol. Solid lines are drawn to represent ±2 standard deviations of log width. Dashed lines extend relationships through complete range of measured log widths.

distributions in the population.

Neither of these techniques gives an exact picture of the cross-sectional shape of the fibers. From structural considerations, it is unlikely that they are bounded by curved surfaces. The shape of the shadow formed by the amosite fiber shown in Fig. 4 suggests that the fiber is rectangular. Shadows similar to this one were observed on many fibers of both amosite and crocidolite. The most common prismatic forms that develop on monoclinic amphiboles are {100}, {010}, and {110}. Electron diffraction indicates that the {100} surface frequently occurs perpendicular to the electron beam.[12] If only {100} and {010} bound the fibers, their cross-sectional shape would be rectangular. If other faces such as {100} are also present, the shape would be somewhat different. Although our data do not provide a conclusive picture of cross-sectional shape, they support the rectangular model as a reasonable approximation.

Within the range of all widths measured, the width to thickness ratio w/t predicted from Eq. (7) varies from approximately 1.0 particles with widths of 0.03 µm to 3.7 for particles width of 1.7 µm. If a rectangular cross section is assumed, calculated fiber volumes are smaller than when circular cross sections are assumed. Therefore, the use of a cylindrical model for fiber geometry[1-3] results in an underestimation in any calculation of the numbers of fibers that occur in a microgram of amphibole asbestos. Similarly, calculations of the concentration of asbestos in air or water expressed in units of nanograms per cubic meter[3-6] overestimate amphibole asbestos if they are based on a cylindrical model.

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